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Experimental measurements on IR emission $(2 < \lambda < 8\mu)$ from nascent ozone formed by the three body recombination $O + O_2 + O_2 \rightarrow O_3^\dagger + O_2$ are reported. This represents an extension of earlier work $(8 < \lambda < 15\mu)$ and covers additional regions of interest:

   a. 4.7μ data on the (101) combination band.

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b. 8μ data possibly due to vibration-rotation transitions of the excited triplet state.

c. A general scan from $2-7\mu$ to look for possible triplet to ground electronic state (forbidden) emission.

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1.0 INTRODUCTION

We have previously reported a number of results from our studies of IR emission from nascent ozone formed by the three body recombination $O + O_2 + M \rightarrow O_3^\dagger + M$ (M = O_2, N_2).[1] These results can be summarized as follows.

1. Emission from the ν_3-mode (8-12μ) implied a quantum efficiency of $\phi(\nu_3) \simeq 0.8$ quanta per recombination; since this result was obtained under the assumption that the ν_1 and ν_3-modes were in V-V equilibrium, the composit result was therefore expressed as $\phi(\nu_1) + \phi(\nu_3) = 1.6$. Also, assuming this amount of vibrational energy was shared intramode to form a Boltzmann distribution, then $T_v(\nu_3) \simeq 1250^\circ K$ was calculated.

2. Emission from ν_3-upper vibrational levels (10-12μ) was substantial and indicated a population in these levels greater than $T_v = 1250^\circ K$ would imply.

3. Measurements on the ν_2 mode (13.5-15.5μ) indicated a quantum efficiency per recombination of $\phi(\nu_2) = 3.7$.

4. The above results account for about 50% of the 1.1 eV exothermicity of this reaction; the remainder presumably goes to the translation, rotation and electronic excitation of the ozone or the collision partner

5. The vibrational relaxation rate for loss of quanta from the mode under observation ($O_3^\dagger + M \rightarrow O_3 + M$, M = O_2, N_2) was measured from these signals.

6. The overall "bulk" recombination rate was also obtained from the data.

All of these results were in the last final report[2] and have recently been published in the open literature.[1] Reference 1 is complete and discusses our results in context with previously published work on ozone recombination.

In the present program, we extended these results by looking for emission from the (101) combination band (4.7μ) and by looking for evidence of the excited (but bound) triplet state predicted by recent theoretical efforts.[3, 4] The combination band is interesting as an independent check on our earlier ν_3 and ν_1-mode measurements and our understanding of the processes involved. In particular, we justified our assumption of

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either equal quantum efficiencies of excitation for ν_1 and ν_3 or rapid V-V coupling between them for our experimental conditions. The triplet state is interesting since it is predicted[3] to be bound by 0.6 ± 0.1 eV, but has not been experimentally detected. It could represent an important channel for recombination since both the triplet and the singlet ground state of ozone correlate with the ground state reactants, viz. $O(^3P) + O_2(^1\Sigma) + M \rightarrow O_3$ (triplet or singlet) $+ M$. As discussed previously,[2] however, we have no quantitative information as to the relative importance of these two channels since although the triplet has more spin states, it also has fewer vibration/rotation states.

Experimentally, we looked for emission both from ν_1 and ν_3 vibration/rotation transitions of the excited electronic states (1-0 transitions predicted[3] at: $\nu_1(8.03\mu)$, $\nu_2(15.8\mu)$ and $\nu_3(8.06\mu)$), and from the (forbidden) triplet to singlet electronic state transitions. These electronic transitions are predicted to be at 0.68 ± 0.2 eV in absorption and 0.38 ± 0.2 eV in emission for transitions beginning in a ground vibrational state.[5] Since our experiment is designed to detect emission, we looked from 2.1 to 6.9μ, realizing that if such emission overlayed a vibration-rotation band, the interpretation would be confused. The f/number was crudely estimated[6] to be on the order of 10^{-8} to 10^{-9}. For our experiment, we then estimated S/N > 10 if the quenching rate implied 10^4 or more collisions.

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2.0 COMBINATION BAND $(W_1 + W_3)$

2.1 Experimental

The experimental apparatus has been well described previously.[1] Briefly, we flash photolyse mixtures of (typically) 0.3% $O_3 + O_2$ at p = 70 to 400 torr, which decomposes over half of the ozone. The $O(^1D)$ formed by the photolysis is quenched to $O(^3P)$ in nanoseconds which then reacts O_2 to make $O_3^\dagger$ (vibrationally excited) in a three-body recombination process, which occurs on the order of 100μ sec. It has been shown that all of our signals are due to excitation resulting from the recombination, with degradation due to collisional quenching, and not from any excited states resulting from the photolysis. Detection at these wavelengths was with an In:Sb detector and filter package which we have utilized previously on another program.[7]

The combination band measurements were made using two filters whose transmission characteristics are shown in Fig. 1 along with a plot of the room temperature emission spectrum of ozone in this region.[8] The $O_3^\dagger$ which is formed quickly establishes a rotational temperature near 300°K, so that for $101 \rightarrow 000$ transitions the emission spectrum should closely resemble this plot; for $202 \rightarrow 101$, $201 \rightarrow 100$, etc transitions this band shape would be roughly preserved but shifted to longer wavelengths due to anharmonicity. The 4.7μ filter provides a basic measurement uniformly covering the band and an adjacent region of longer wavelengths. The 5.1μ filter sees mainly the P-branch and longer wavelengths and was used to get some indication about upper level excitations.

2.2 Results - 4.7μ Filter

Unlike our previous work at longer wavelengths, in these measurements the IR detector initially responds to scattered emission from the flash lamps. This is despite substantial baffeling and is the result of light directly transmitted by the quartz envelope of the flash tube. At longer wavelengths, the quartz acts to filter such light and one has only thermal emission from the surface of the envelope. This can be seen in Fig. 2 where we display oscillograms of 4.7μ measurements. In order to extract as much information as possible from the data, we verified the reproducibility of the flash recovery in pure N_2, and then point-by-point subtracted the N_2 "signals" from the signals coming from the $O_3 + O_2$ mixtures. This difference in signals $S(O_3) - S(N_2)$ was attributed to $(\nu_1 + \nu_3)$ combination band emission. In contrast to our earlier work at 9.6μ, we were not able to see the time to peak signal (t_{max}) or the value of the peak signal due to excessive flash lamp light at these early times. We did measure the signal at times $\geq 3t_{max}$ to obtain the overall recombination rate (as illustrated in Fig. 2) and to obtain by extrapolation, if necessary, the signal level at
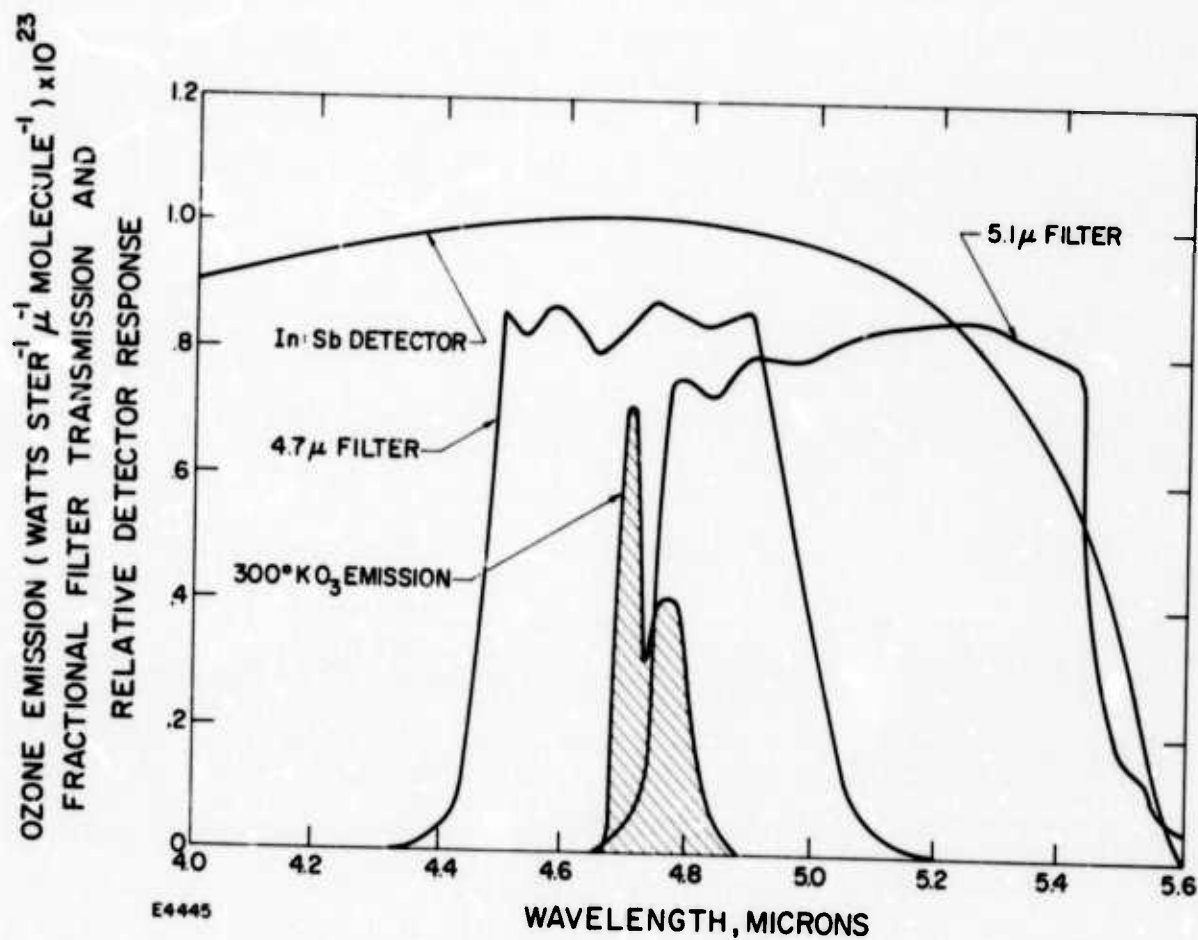
Fig. 1   Spectral Transmission of 4. 7 and 5. 1μ Filters, Relative
Response of the In:Sb Detector, and the Emission Spectrum
for 300°K Ozone

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4.7μ FILTER

EMISSION 100 μV/CM

S_{N_2}

S_{O_3}

O_2+ 0.28% O_3

0   200   400   600   800

TIME, μSEC

$\dfrac{S_{O_3}-S_{N_2}}{(S_{O_3}-S_{N_2})_{100\mu SEC}}$

1.

0.1

0.6

0   200   400   600   800   1000

TIME, μSEC

E 4486
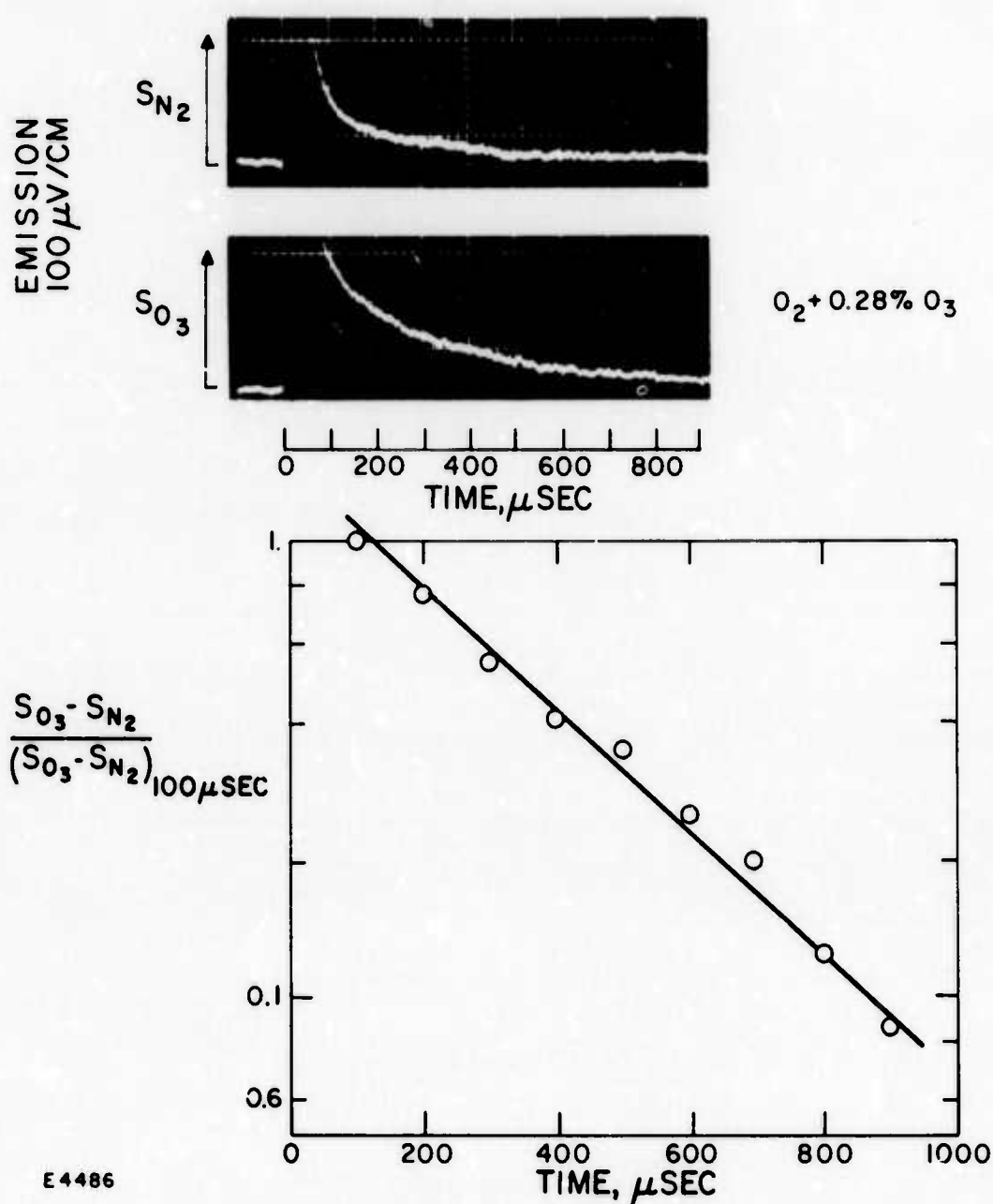
Fig. 2   Oscillograms of 4.7μ Signals in Pure N_2 at 100 Torr Showing
Recovery of In:Sb Detector from Scattered Flashlamp Light,
and in 100 Torr of 0.28% O_3 + O_2 Showing Additional Signal
Due to Ozone ($\nu_1 + \nu_3$) Combination Band Emission.   The
difference of the signals is plotted vs time on a semi-log plot,
and the slope of the straight line implies a rate for $O + O_2 +$
$O_2 \rightarrow O_3 + O_2$ of 2.9 x 10^{-34} cm^6 sec^{-1}.

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$t = 3t_{max}$. Our detector was also calibrated with a blackbody standard radiation source so the absolute signal levels could be compared to predictions based on our earlier ν_3-mode measurements. [1]

In all of this work, a quasi-steady state is established in a time scale of order of the vibrational relaxation time for the process $O_3^{\dagger}$ + $M \rightarrow O_2 + M$ (where the dagger indicates vibrational excitation in the mode under observation, and relaxation is out of this mode to translation or to another mode of the same or the colliding molecule). The steady-state represents a balance between the three body formation reaction (rate constant k_1) and the sum of the quenching reactions (rate constant k_2). Thus, as the initial O-atoms (formed by the flash) are consumed, the signal decays with a time constant determined by the overall bulk recombination rate, since this is what controls the rate of loss of O-atoms. The formalism is given in Section III of Ref. 1. The fact that we obtain k_1 (recombination) = $3.12 \pm 0.61 \times 10^{-34}$, in agreement with our earlier result, is further confirmation that these signals are due to the processes described. For completeness, the data are shown in Fig. 3 for both the 4.7μ, 5.1μ and a combination of these two filters in series (the signals at 70 torr were of quite low signal-to-noise and their scatter is therefore not too disturbing).

In general, we read absolute signal magnitudes at $t = 3t_{max}$. Exceptions occurred in the higher pressure cases when we extrapolated the signals, in plots such as in Fig. 2, back to $3t_{max}$. [10] For purposes of analysis and display, it was convenient to utilize this procedure as opposed to comparing runs at different pressures at different times. We justified this extrapolation for our conditions by plotting the expected signal behavior vs t/t_{max} for various pressures. The quantity (f/f_{max}) which is plotted, varies with time according to $[\exp(-R_1 t) - \exp(-R_2 t)]$ where $R_1 = k_1 [O_2]^2$ and $R_2 = k_2 [O_2]$ with $k_1 = 3 \times 10^{-34}$ cm^6 sec^{-1} and $k_2 = 2 \times 10^{-14}$ cm^3 sec^{-1}, which are the values we previously obtained. [1] In Fig. 4 this is shown and it can be seen that for $t \geq 3t_{max}$ the signal behaves linearly on a semilog plot.

The results of our measurements with the 4.7μ filter are given in Fig. 5. This figure is analogous to Fig. 7 of Ref. 1 except that data are given for $t = 3t_{max}$ rather than t_{max}. The solid line through the data has a calculated pressure dependence and is scaled by observation to best fit the data. This line is taken to represent $[101]/[O]_0$ at $t = 3t_{max}$ from our present data. The dashed line shows our previous results for $[001]/[O]_0$ at t_{max} from which the broken line is obtained by our model of the signal vs time behavior. The ratio of $([101]/[O]_0)3t_{max}$ to $([001]/[O]_0)3t_{max}$ is just $[101]/[001] = e^{-\Theta/T_v}$ where Θ (°K) $= 1.438 \times (\nu_{101} - \nu_{001}$ cm$^{-1})$. Thus, we obtain a vibrational temperature $T_v = 1200$°K from these present results. The sensitivity of T_v to the data is illustrated by the numbers on Fig. 5. This is essentially the same vibrational temperature we obtained using our ν_3-mode data in the earlier work [1] (1250°K) and indicates its adequacy for understanding the population distribution among the lowest few levels. As we saw previously, however, and will see with our 5.1μ data here, the higher vibrational levels are populated in excess of what would be predicted using $T_v = 1200$°K.

Fig. 3   Recombination Rate Data vs Total Pressure for $O + O_2 + O_2 \rightarrow O_3 + O_2$ Obtained from Data such as Shown in Figs. 2 and 6 and Using the 4. 7 and 5. 1μ Filters in Series
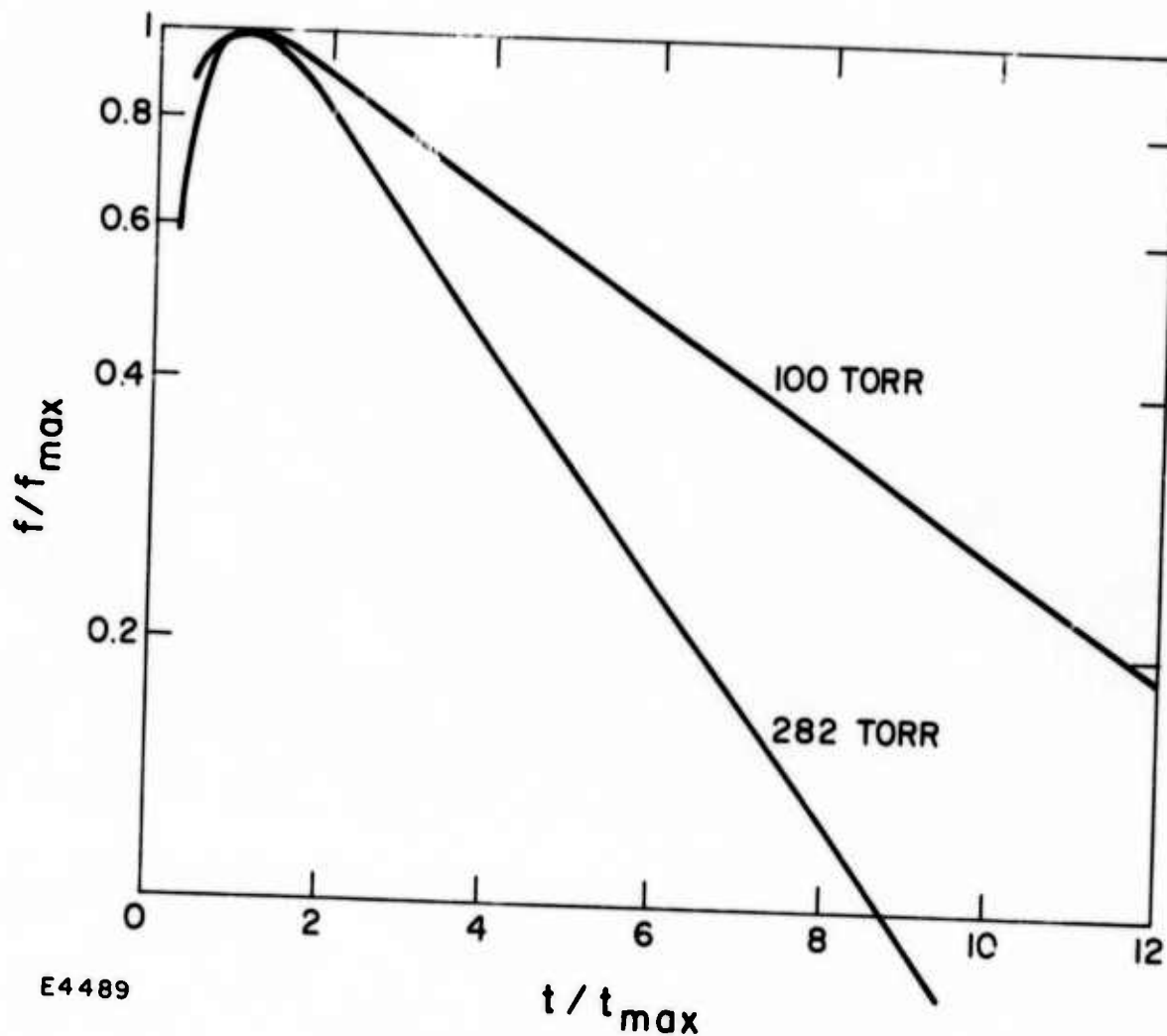
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Fig. 4 $f/f_{max} = [001]/[001]_{max}$ are plotted vs t/t_{max}. These values of f are calculated based on the simple theoretical frame work utilized in Ref. 1 and show that our signals are certainly expected to decay exponentially for $t/t_{max} \geq 3$.
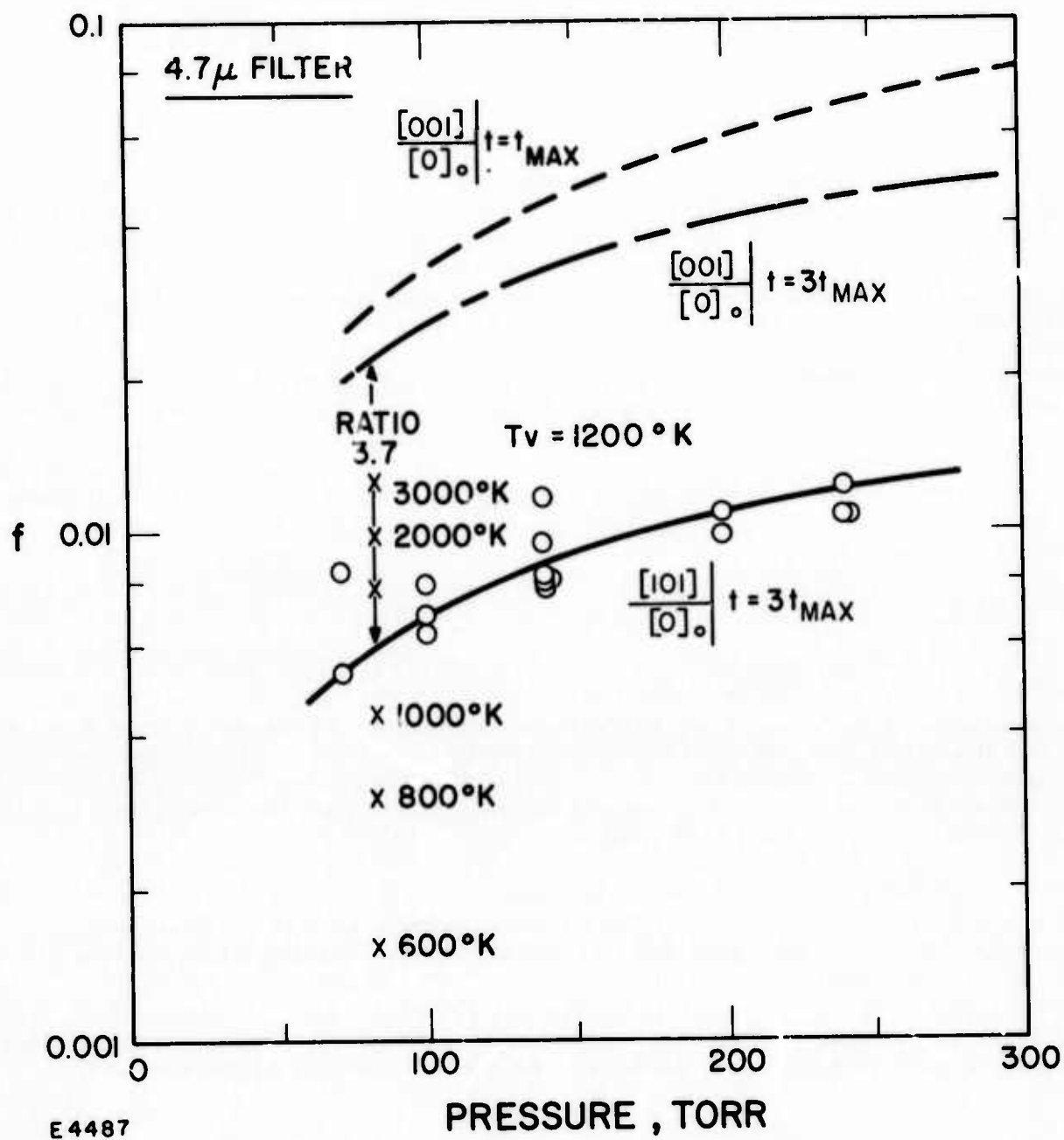
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Fig. 5   Reduced data for $[101]/[O]_0$ at $t = 3t_{max}$ are shown vs total pressure. Solid line is our fit to this data. Dashed line represents our earlier data for $[001]/[O]_0$ at $t = t_{max}$, and broken line is this earlier data theoretically scaled to $t = 3t_{max}$. Ratio of broken to solid line implies a $T_v \simeq 1200^\circ K$.

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Our largest uncertainty in these measurements is the O-atom concentration, $|O|_0$, for two reasons. Firstly, O-atoms are obtained both by photolysis $O_3 + h\nu \rightarrow O(^1D) + O_2 (^1\Sigma) + O_3 \rightarrow O(3P) + 2O_2$, and the amount of $O_2 (^1\Sigma)$ formed in the flash is a subject of debate in the literature.[11] Secondly, we have conflicting data in this present work on the amount of primary photolysis. Considerable attention was given to this problem in our previous work, and we rather consistantly measured 30 to 35% primary photolysis. This data is obtained separately from the IR measurements by use of $O_3 + N_2$ mixtures for reasons discussed earlier.[1] In the present case we took our 4.7μ data, and then, for convenience, obtained ν_3 mode (9.6μ) data to check our photolysis by reference to our earlier work. We obtained 21% photolysis which seemed reasonable for "old" flash lamps. Subsequently (a month later) when our flash lamps began to give difficulty with pretriggering, we measured, using an $O_3 + N_2$ mixture, a primary photolysis of 49% which seems much too high based on all our earlier results.[12] We have arbitrarily used the average of these two determinations (40%) in our data reduction for results during this period.

These data were checked for self-absorption in the manner discussed in Appendix B of Ref. 1, and a correction factor of 22% is utilized in reduction of the data.

2.3 Results 5.1μ Filter

A few runs were made with the 5.1μ filter and that data is illustrated in Fig. 6. Here we put both the N_2 (recovery of the detector from the flash) and the $O_3 + O_2$ traces on the same oscillogram so that the difference between the signals can be more easily obtained. Because of the longer wavelength bandpass of this filter, there is less flash lamp light picked up by the detector. Again, we obtained a bulk recombination rate consistent with our earlier work ($\sim 3 \times 10^{-34}$ cm^6 sec^{-1}).

Including the appropriate absolute calibrations, the power incident on the detector with the 5.1μ filter was comparable to that obtained with the 4.7μ filter. Considering the degree of overlap with the band, shown in Fig. 1, this seems surprising. Qualitatively, however, it could be interpreted in terms of upper level vibrational excitation, in agreement with our past results using the "ν_3-upper levels" filter. This interpretation is not the only one possible, however, as we will discuss in Section 4.0.
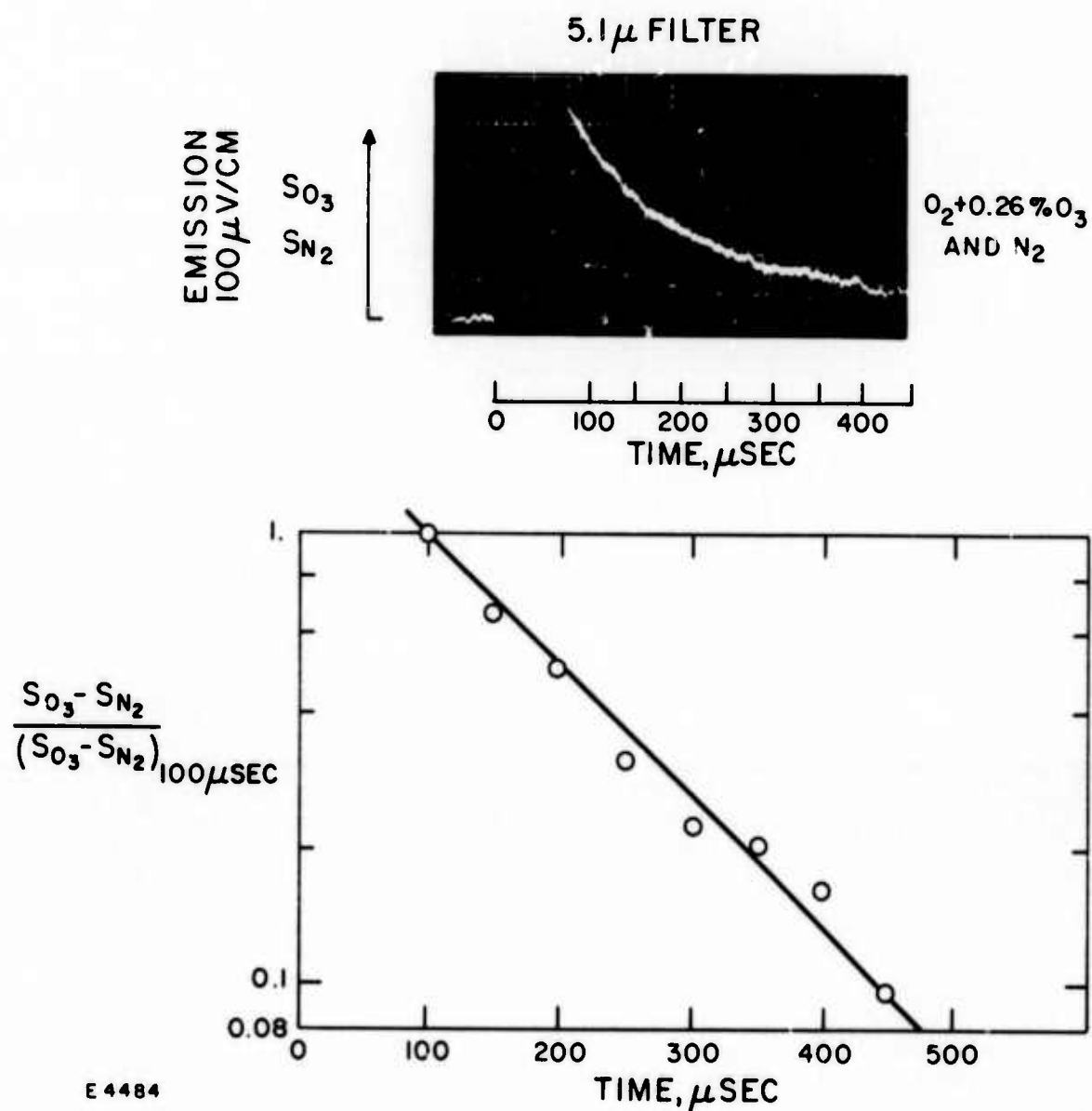
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Fig. 6 Oscillogram of Two Superimposed 5.1μ Signals in Pure N_2 at 141 Torr, Showing Recovery of In:Sb Detector from Scattered Flashlamp Light, and in 141 Torr of 0.26% O_3 + O_2 Showing Additional Signal Due to Ozone ($\nu_1 + \nu_3$) Combination Band P-Branch and Upper Levels Emission. The difference of the signals is plotted vs time on a semi-log plot, and the slope of the straight line implies a recombination rate of 3.2×10^{-34} and $cm^6 sec^{-1}$.
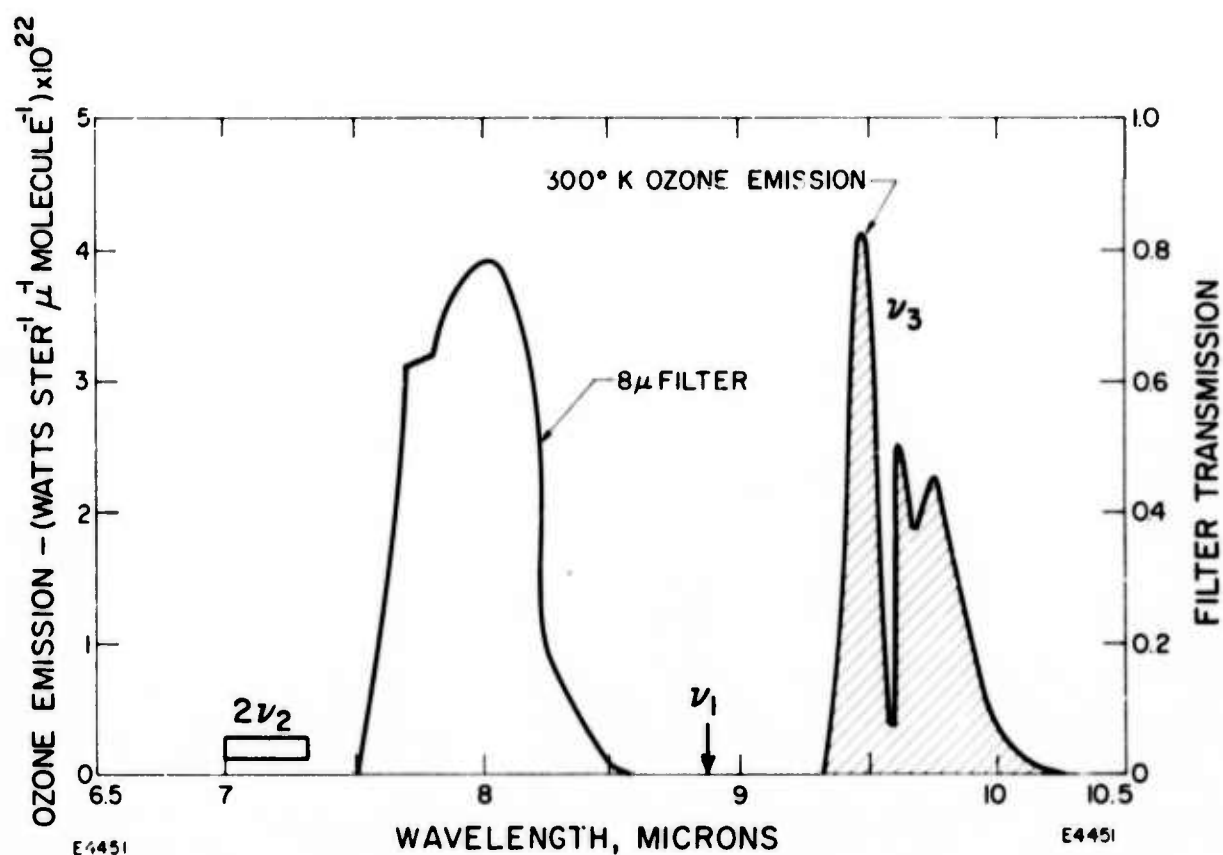
Fig. 7   Spectral Transmission of 8μ Filter used to Look for ν_1 and ν_3 Vibration-Rotation Transitions of the $^3B_2$ State. Their predicted positions are indicated. A 300°K emission spectrum due to the ground state ν_3-band is also shown for comparison. The ν_1 band has a peak value of 2.5×10^{-24} watts $ster^{-1} \mu^{-1}$ molecule^{-1} at the location indicated. The location of the $2\nu_2$ band is also shown.

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3.0 EXCITED STATE ν_3 AND ν_1 V-R TRANSITIONS - 8μ

Data were obtained in the same cell configuration but using a special Cu:Ge detector with cold-shield, filter, lens and MOSFET preamplifier (all at 5°K) that had been developed for our earlier work.[1] The spectral response of this filter at room temperature is shown in Fig. 7 along with the 300°K emission spectrum of ozone calculated using the AFCRL computer tape of ozone lines.[9] This filter curve will shift to shorter wavelengths when cooled to 5°K by about 1 to 3% according to its manufacturer. The filter was used in series with SrF_2 chosen to provide additional blockage against long wavelength transmission. It clearly does not intercept the ground state ν_1 or ν_3 bands, and of course their higher level V-R transitions are shifted to longer wavelengths. The $2\nu_2$ combination band, which lies just out of the bandpass at shorter wavelengths, has been shown by McCaa and Shaw[13] and it appears weak; its strength however, has not been given, as confirmed in a recent conversation.[14] We have estimated its value, based on the scan shown in Ref. 13 and comparison to adjacent measured bands, at $S = 0.14$ ama^{-1} cm^{-2}. At this value it should clearly make no contribution in the present work.

With pure N_2 there was only a very weak transient signal measured (0.1 mv peak at t $\simeq 25\mu$ sec after flash initiation), indicating very minor response to scattered (probably thermal) photons from the flash lamps. With $O_3 + O_2$ mixtures small signals were recorded as illustrated in Fig. 8. There is an initial 10μsec loss of the trace due to electrical pickup (compare Fig. 4 of Ref. 1), but then the signal rises to a peak and decay as O-atoms are depleted. This final decay time was consistent with normal three-body recombination as the mechanism for overall O-atom depletion. Qualitatively, it decreased with increasing pressure, but signals were too noisy to see if it demonstrated the expected pressure squared dependence. The peak signal (S_{max}) was read, and after subtracting the corresponding nitrogen signal S_{N_2} of 0.1 mV it was plotted vs the product of total pressure and initial ozone concentration. This is appropriate if the signal is proportional to $[O_2] \times [O]$ (since $[O] \propto$ initial P_{O_3}) as it is in the simple theoretical model we have utilized thus far in presenting our results.[1]

There is a difficulty in further quantitative reduction of this data in that we do not definitely know its origin. Since there are no absorption features of room temperature ozone in this bandpass, then vibration-rotation transitions of the bound triplet state seems like a good hypothesis. If this is the explanation, then we need the radiative decay time for $^3B_2$ ($\nu_3 = 1$) $\rightarrow$ $^3B_2$ ($\nu_3 = 0$) to properly deduce the concentration of $[O_3^{*\dagger}]$ (asterisk * denoting $^3B_2$ electronic and dagger $\dagger$ denoting vibrational

8μ FILTER

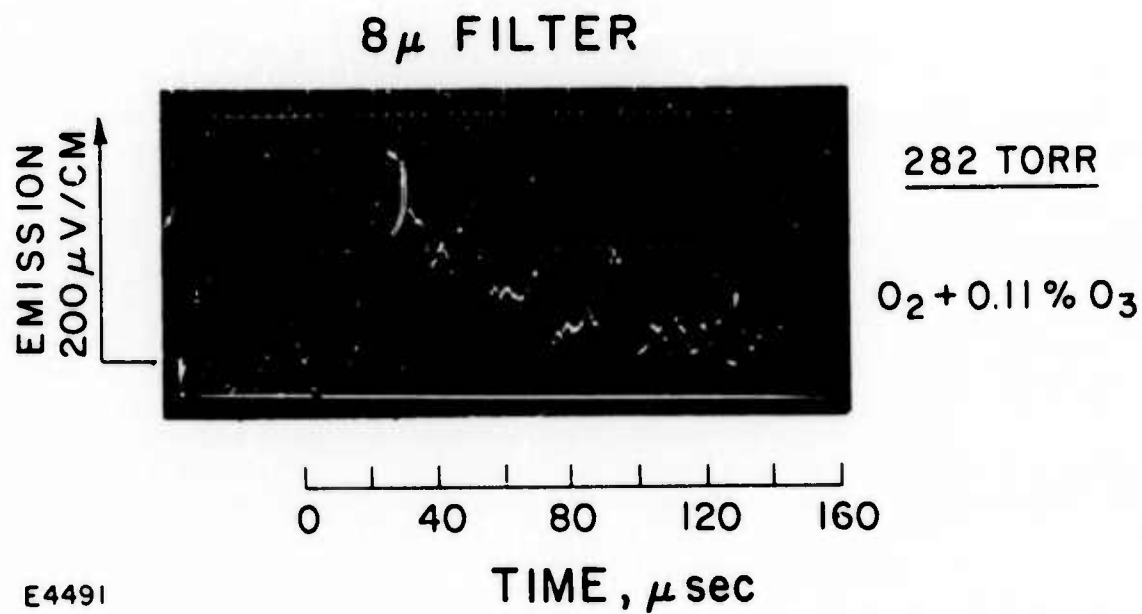EMISSION 200 μV/CM

282 TORR

$O_2 + 0.11\% O_3$

E4491

TIME, μ sec

Fig. 8 Oscillogram of 8μ Emission in 282 Torr of 0.11% O_3 + O_2.

For this run the final decay time implies $k_1 = 2.5 \times 10^{-34}$ and the time to the peak implies a quenching rate $k_2 = 2 \times 10^{-14}$ cm^3 sec^{-1}.

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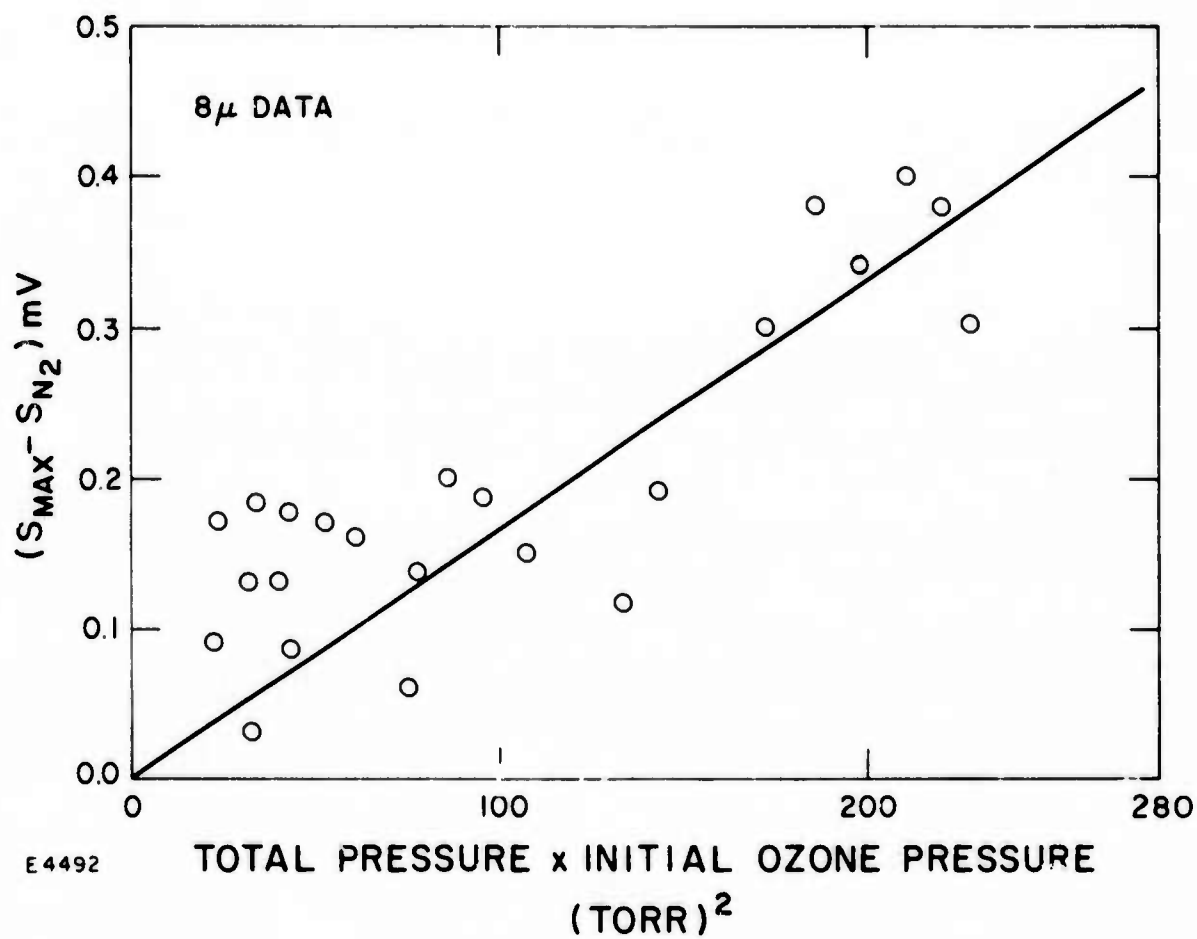Fig. 9   Peak Signal in $O_3 + O_2$ Mixtures Minus the Signals in Pure N_2 (Due to Flashlamp Effects) Plotted vs (Total Pressure)* (Initial Ozone Pressure) as Measured for Each Run

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excitation). Loss of $O_3^{*\dagger}$ can be by either electronic or vibrational de-excitation and presumably only collisional quenching is important for our 100μ sec time scale. [15]

If we arbitrarily use 94 msec (the $^1A_1$ ν_3-mode radiative lifetime) for

$$O_3^{*\dagger} \xrightarrow{\tau_{8\mu}} O_3^* + h\nu$$
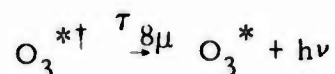
and the formalism given in Ref. 1, then we obtain a quantum efficiency for

$$O + O_2 + O_2 \rightarrow O_3^{*\dagger} + O_2$$
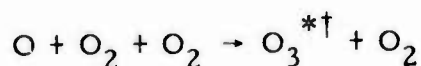
of $\phi^{*\dagger} = 0.011$. It must be remembered that ϕ^*, the quantum efficiency for electronic excitation without regard for simultaneous vibrational excitation is not implied by this number, except that $\phi^* \geq \phi^{*\dagger}$. To obtain ϕ^*, one needs to observe $^3B_2 \rightarrow {}^1A_1$ electronic emission summed over all vibrational levels.

It should also be noted that the time to peak signal in the 8μ data implies a quenching rate constant for removal of $O_3^{*\dagger}$ by the process

$$O_3^{*\dagger} + M \xrightarrow{k_q^*} O_3^\dagger + M$$

or

$$O_3^{*\dagger} + M \xrightarrow{k_q^\dagger} O_3^* + M$$
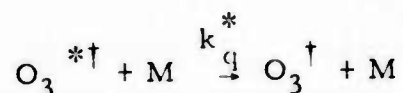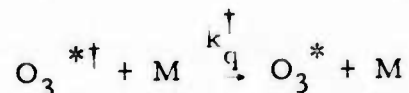
of k_q^* or $k_q^\dagger$ approximately equal to 2×10^{-14} cm^3 sec^{-1}, which curiously is the same value we obtain for relaxation of ground state vibrational levels. [1]

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4.0 WAVELENGTH SCANS 2.6 - 6.5μ

The vertical spacing between the lowest ozone potential energy surfaces is predicted to be 0.38 eV at the $^3B_2$ equilibrium geometry with a "safe" uncertainty quoted as 0.2 eV and a comment that the 0.38 eV figure is probably a little high.[5] This value of 0.38 eV ± 0.2 eV converts to 3.3μ with bounds of 2.1 and 6.9μ. Since we are looking for emission, it is this number, and not the 0.68 eV spacing at $^1A_1$ equilibrium geometry, which is appropriate.

For these scans we used a wavelength calibrated room temperature circular-variable-filter (CVF) together with our Cu:Ge detector. The detector utilized sapphire as a cold blocking filter to cut off around 6.5μ and thereby minimize thermal background noise. The CVF filter has a spectral resolution of $\Delta\lambda/\lambda \simeq 0.8\%$ where $\Delta\lambda$ is the full width at half max. In fact we did not have our detector element focused on the CVF so as to attain this resolution, but rather we operated with (measured) $\Delta\lambda/\lambda \simeq 2.5\%$. Our earlier wavelength calibration was checked by scanning a filter of known bandpass and found to be within 0.05μ. The detector plus CVF plus system of viewing apertures was calibrated using a standard blackbody radiation source.

The results of these scans were that we did not see any signals we could attribute to O_3^*. We display the essence of the results in Fig. 10 by showing the bounds we were able to obtain with these scans at the radiation that could have been coming from O_3^*. Figure 10 also has the results of all our other measurements plotted so as to demonstrate their bandpass (full width at half max) and their relative magnitudes.

Our greatest restriction was probably due to the intrinsic 0.8% spectral resolution of the CVF and the fact that we were searching for a band emission of (estimated) low S/N. Given that the width of a normal vibration-rotation band (e.g., see Fig. 1) is $\Delta\lambda/\lambda \sim 5\%$ with probable spreading due to upper level excitations, and presumably additional spreading if coupled with an electronic transition then a resolution like 10% or greater would be more useful. Because of this we also did additional searching using various fixed bandpass filters. In particular, we used filters with bandpasses (1.97 - 2.46μ), (2.35 - 3.05μ), (3.64 - 4.85μ), (4.18 - 4.61μ), (4.41 - 4.93μ - the "4.7μ filter"), (4.75 - 5.43μ - the "5.1μ filter"), and (5.67 - 7.45μ - the "6.6μ filter"). There was no significant new information from this effort except for the signals obtained using the 6.6μ filter.[16] These signals are in a region presumably free of normal ground state band emission, and yet as can be seen in Fig. 11 they qualitatively increase in magnitude and in rate of decay with pressure. The final decay rate is within a factor of two of the expected rate of recombination but beyond that not much can be said. The decay does not look exponential, but then the signals are rather noisy.
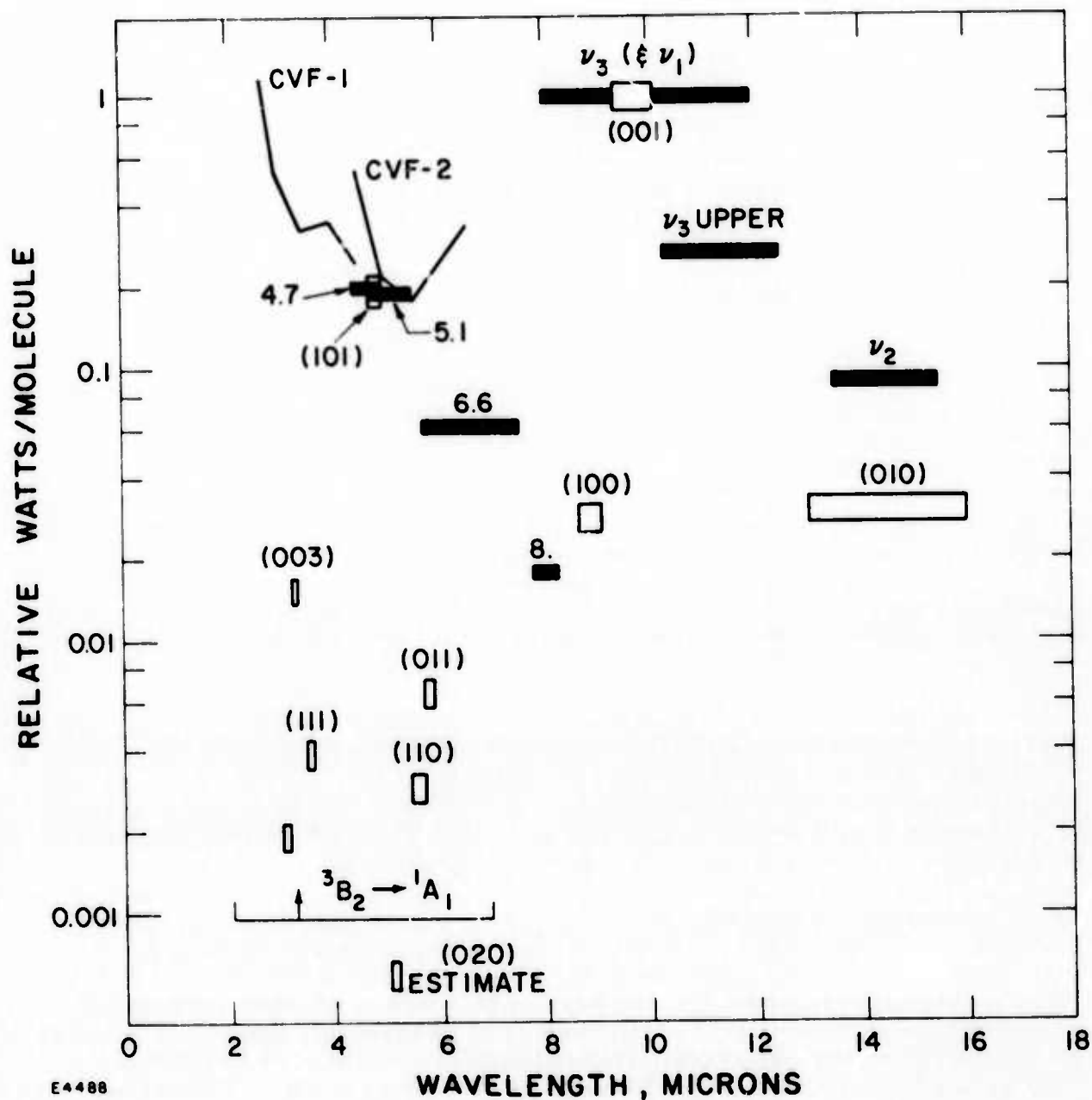
Fig. 10   Spectral Intensity vs Wavelength for Ozone Bands at 300°K are shown with this Plot (Open Rectangles - FWHM is Indicated by the Spectral Extent while Relative Heights are Scaled by their Predicted Relative Emissions for T_v = 1300°K). Also shown are relative powers incident on a detector in our experiments at 200 torr for the various filters we have used (solid rectangles - FWHM is indicated by the spectral extent).
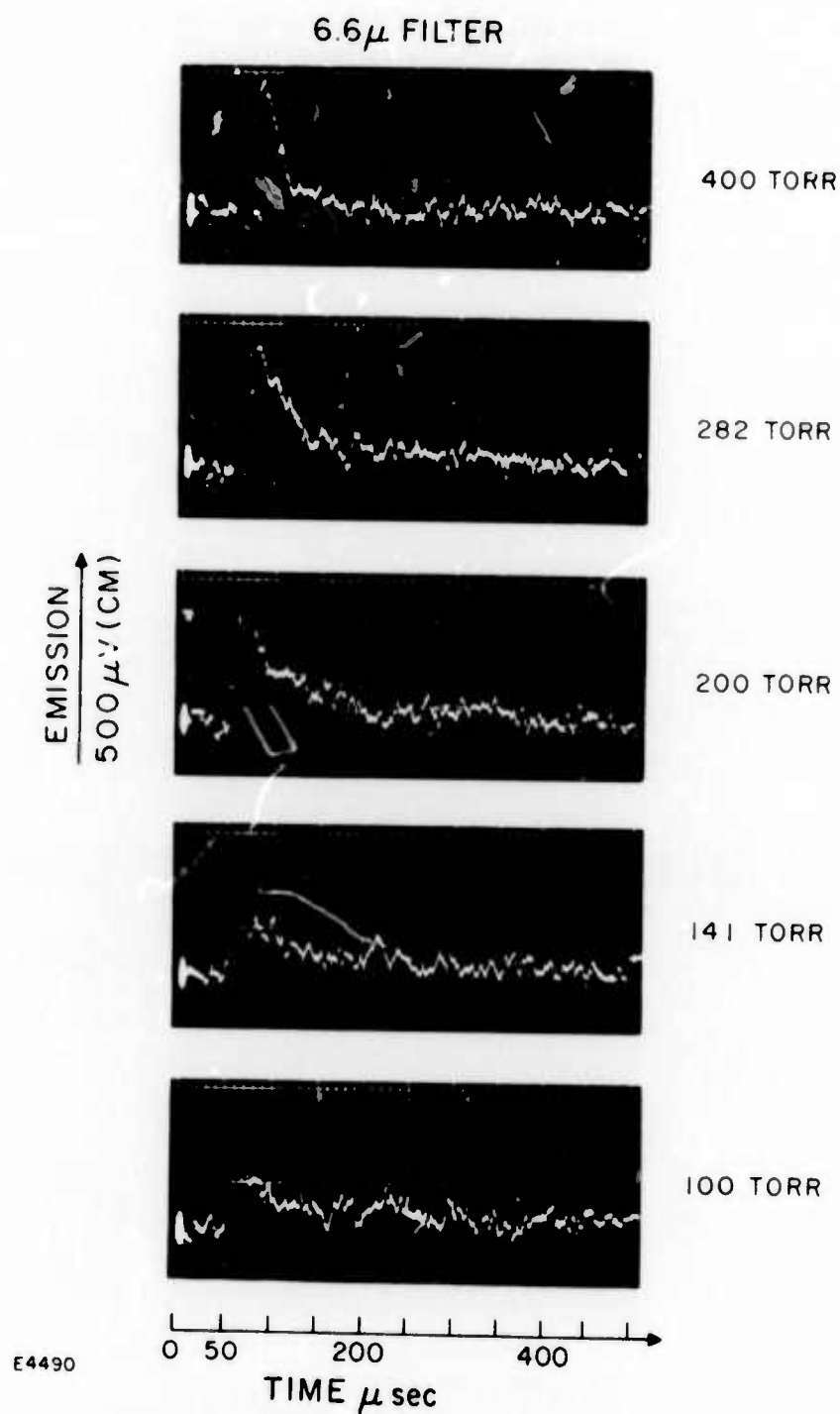
Fig. 11   Oscillograms Showing Signal Behaviour vs Pressure for the 6.6μ Filter

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The intriguing question is what generates the 6.6μ signals. They could be due to $^3B_2 \rightarrow {}^1A_1$ transitions, or they could be part of a recombination continuum, which has been recently proposed. [17] If the latter does exist it would be desirable to characterize its intensity and spectral dependence to find what contribution it may make in other spectral regions.

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10. t_{max} α(pressure)$^{-1}$ (see Eq. 6 of Ref. 1) so that at sufficiently high pressure even $t = 3t_{max}$ merges into the region where the detector is recovering from the flash lamp light pulse.

11. We use 70% in our analysis so that our "initial O-atom concentration" $[O]_o$ is equal to the number of O-atoms obtained from the "primary photolysis" multiplied by 1.7 providing $[O]_o \leq [O_3]$ in the initial mix before the flash. In addition a small number of O-atoms are formed by photolysis of the O_2 via its Schumann-Runge absorption band which just overlays the quartz flash lamp envelope around 1800 $\overset{\circ}{A}$. These represent about a 10% contribution.

12. In addition, we then installed new lamps and measured a primary photolysis of 69% for them -- which is larger than we have ever previously measured.

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15. Radiative lifetimes at these wavelengths are typical of the order of 10 msec or longer. Our measurement of ground electronic state vibrational relaxation, however, gives $\tau \simeq 8\mu$ sec at 200 torr.

16. Measurements at the shorter wavelengths are difficult due to initial flash lamp scattered radiation; there may be significant signals obscured during this interval. Further work would profit from development of a fast shutter for the detector.

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